Mixed-valent ground state of CeO$_2$

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The electronic ground state, core-hole states, and valence-hole states of CeO$_2$ are studied taking into account strong correlation among the $4f$ electrons. The ground state is considered as a mixture of two configurations, $4f^0$ and spin-singlet totally symmetric $4f^1$-O $2p$-hole states. By an analysis of the core-level photoemission spectrum, the $4f$ occupancy is obtained to be about 0.6. The possibility of this mixed-valence mechanism in metallic mixed-valent systems and α-Ce is also discussed.

Cerium exhibits fascinating physical and chemical properties due to the $4f$ electrons.[1] The nature of electronic states associated with the $4f$ electrons, however, are far from well understood except for the localized $4f^1$ configuration of the Ce^{3+} ion. In so-called mixed-valent compounds [CeN (Refs. 2–4), CePd$_3$,[5] etc.], magnetic properties, lattice volumes, etc., show anomalous behaviors arising from the $4f$ occupancy less than unity. Mechanisms suggested for the mixed valency have been based on the mixing of two configurations, $4f^0(5d6s)^m \rightleftharpoons 4f^1(5d6s)^{m-1}$, where $(5d6s)^m$ is m electrons in the conduction band, and therefore $4f^1$ should be located close to the Fermi level.

Recently, questions have been raised against the existence of purely tetravelent (Ce^{4+}, $4f^0$) compounds by photoemission,[6] x-ray spectroscopy,[7] etc., suggesting the presence of $4f$ electrons in tetravalent compounds; even in CeO$_2$, which has been regarded as an obvious example of $4f^0$, x-ray spectroscopy showed $4f^1$-derived features as well as $4f^0$ ones.[7,8] This argument was criticized by some authors[8] in that the $4f^1$ signal could arise from the $4f^0$ initial state by a strong perturbation of a core hole.

The insulating, nonmagnetic properties of CeO$_2$ are most naively understood as due to the tetrapositively ionized Ce ion $(4f^0)$ and completely filled O $2p$ valence band. However, $4f^1$ and a valence-band hole (L^{-1}) can form an exciton-like complex with the same symmetry as the $4f^0$ configuration, that is, spin singlet with the full spatial symmetry. This configuration $4f^1 L^{-1}$ is close in energy to the $4f^0$ configuration, and mixing of the two configurations $4f^0 \rightleftharpoons 4f^1 L^{-1}$ should be considered in the initial ground state. In this Communication, a quantitative analysis of the core-level x-ray photoemission (XPS) spectrum of CeO$_2$ (Ref. 9) has been performed based on this idea, taking into consideration also final-state effects due to a core hole, and the $4f$ occupancy has been obtained to be about 0.6. The present method holds for other tetravalent compounds such as Ce(TMHD)$_4$, where TMHD denotes tetramethylheptane dionate, BaCeO$_3$,[9] and semiquantitatively for metallic CeRh$_3$, CeRu$_2$,[6] CeCo$_5$,[8] etc.

The $4f$ electron number thus determined is larger than has been estimated for lattice volumes, and suggests that most of tetravalent Ce compounds are mixed valent rather than pure $4f^0$. We would like to point out the possibility that this type of mixed-valent mechanism is dominant even in some metallic mixed-valent systems and also in α-Ce. As the mixing between the $4f^0$ and $4f^1 L^{-1}$ states is caused by hybridization between the $4f$ and ligand (L) orbitals, small volumes favor the total energy of the "bonding"

$4f^0 + 4f^1 L^{-1}$ ground state.

While the core-level XPS spectra of La, Ce, Pr, and Nd compounds with stable valence show simple structures, the main line and a $L \rightarrow 4f$ satellite,[10] the core levels of CeO$_2$ exhibit complex features.[9] The Ce $3d$ spectrum of CeO$_2$ is shown in Fig. 1, where each spin-orbit component (separated by Δ_{so}) has two intense peaks (v and v''' for $3d_{5/2}$ and u and u''' for $3d_{3/2}$) separated by ~ 16 eV and weak satellites (v' and v'' for $3d_{5/2}$ and u' and u'' for $3d_{3/2}$) near the low binding energy peak. In the original assignment,[9] the ground state was considered to be $4f^0$. The v''', u''' and v,u were identified with the main and $L \rightarrow 4f$ $(4f^0 \rightarrow 4f^1 L^{-1})$ shake-down transitions, respectively, but the weak features v', v'', u', and u'' could not be explained.
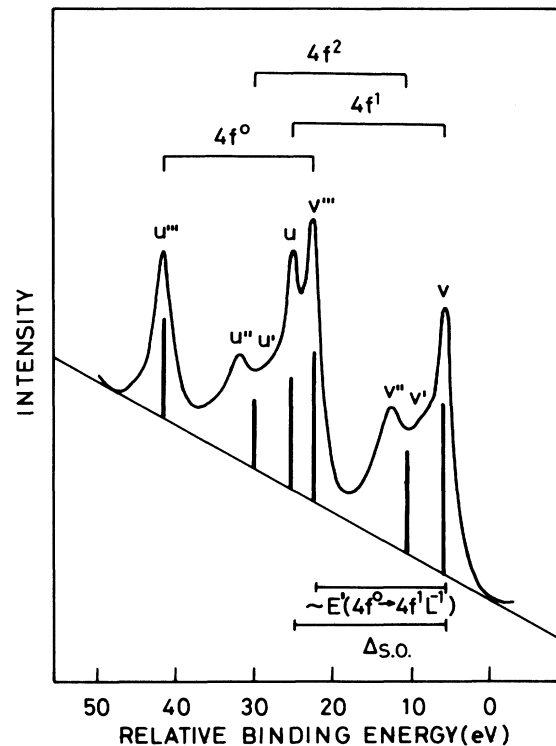

FIG. 1. Ce $3d$ core-level XPS spectrum of CeO$_2$ (Ref. 9) and calculated spectrum (vertical lines) with use of parameters in the text. Principal components in the final-state peaks are indicated by $4f^0$, $4f^1$, and $4f^2$.

A recent molecular-orbital calculation on the CeO_8^{12-} cluster with use of the scattered-wave $X\alpha$ (SW-$X\alpha$) method[11] attributed the weak satellites to shake-up ones accompanying the main lines u and v, but could not give reasonable explanation to the intense high binding energy peaks v''' and u'''. Although self-consistent, local-density, one-electron calculations may be useful to derive some ground-state properties such as the $4f$-electron number,[12] it is not appropriate for excited states of $4f$ systems in which electron correlation is important.

We therefore expand the initial and final states of the CeO_8 cluster using a basis set with the integral $4f$ number n, and for the energetic reason neglect $n \geq 2$ in the initial state and $n \geq 3$ in the final state. Thus the initial ground state is given by

$$\Psi_I = c_{I0}|0\rangle + \sum_l c_{Il}|l\rangle , \tag{1}$$

$$|l\rangle = \alpha_l^\dagger|0\rangle = \sum_{ij} \Gamma_{ij}^l \sum_\sigma f_{i\sigma}^\dagger L_{j\sigma}|0\rangle , \tag{2}$$

where $|0\rangle$ represents the $4f^0$ configuration with the completely filled $O\,2p$ levels, $L_{i\sigma}^\dagger$ and $f_{i\sigma}^\dagger$ are creation operators for the spin-σ ligand orbital L_i and the spin-σ crystal-field level f_i of $Ce\,4f$, respectively, and Γ_{ij}^l's are coefficients to make the $4f^1 L^{-1}$ state fully symmetric. The SW-$X\alpha$ results have shown that only the $4f\,a_{2u}$-$L\,a_{2u}$ overlap and one of the two $4f\,t_{1u}$-$L\,t_{1u}$ overlaps are important, and we include these two terms ($l = a_{2u}$ and t_{1u}) in (2). $\langle 0|H|l\rangle \equiv V_l$'s, where H is the Hamiltonian of the system, can be evaluated from the SW-$X\alpha$ calculations as $\langle 0|H|a_{2u}\rangle \equiv V_1 = 1.48$ eV and $\langle 0|H|t_{2u}\rangle \equiv V_2 = 1.71$ eV.[13] The final core-hole state should also be a singlet state apart from the core-hole degeneracy by neglecting $3d$-$4f$ multiplet coupling and is given by

$$\Psi_F' = c_{F0}|0'\rangle + \sum_l c_{Fl}|l'\rangle + \sum_{lm} c_{Flm}|lm'\rangle , \tag{3}$$

$$|l'\rangle = \alpha_l^\dagger|0'\rangle , \tag{4}$$

$$|lm'\rangle = \alpha_l^\dagger \alpha_m^\dagger|0'\rangle , \tag{5}$$

where primes denote the presence of a core hole. In the third term of (3) there is only one term $|a_{2u}t_{1u}'\rangle$;

$$\langle 0'|H|a_{2u}'\rangle = \langle t_{1u}'|H|a_{2u}t_{1u}'\rangle = V_1$$

and

$$\langle 0'|H|t_{1u}'\rangle = \langle a_{2u}'|H|a_{2u}t_{1u}'\rangle = V_2 .$$

X-ray photoemission spectroscopy (XPS) intensities are calculated with use of the sudden approximation

$$I_F \propto |\langle \Psi_I'|\Psi_F'\rangle|^2 . \tag{6}$$

An energy required to move one electron from $O\,2p$ to $Ce\,4f$ in the core-hole state may be estimated by the $Z+1$ approximation:

$$E'(4f^0 \rightarrow 4f^1 L^{-1}) \equiv E_1 \sim -15 \text{ eV}$$

and

$$E'(4f^1 L^{-1} \rightarrow 4f^2 L^{-2}) \equiv E_2 \sim 0 \text{ eV} .$$

In the ground state, $E(4f^0 \rightarrow 4f^1 L^{-1}) \equiv E_0 \sim 0$ eV. The energy difference between $O\,2P\,a_{2u}$ and t_{1u} is only 0.1 eV (Ref. 11) and has been neglected. These three parameters were adjusted around the above values to give best fit to the energies and intensities of the XPS: $E_1 = -14.2$ eV, $E_2 = 1.1$ eV, and $E_0 = 0.1$ eV. The spectrum thus obtained

is shown in Fig. 1. One can see that the calculated spectrum reproduces quite well the experimental one. The most significant result is that the $4f$ number is as large as 0.61, which is nearly the same as that obtained for the SW-$X\alpha$ ground state and is considerably larger than that widely accepted ~ 0. This value is compared with that inferred from the x-ray absortion[7] (0.68). With use of the above parameters the ground state (1) is calculated to be 2.2–2.3 eV below pure $4f^0$ and nonsinglet $4f^1 L^{-1}$ states, consistent with nonmagnetic behavior at experimental temperatures.

Based on the above scheme, the $4f$-derived resonant photoemission spectrum is also calculated. The valence-hole state with the i symmetry is expressed as

$$\Psi_{Fi} = c_{Fi}L_{i\sigma}|0\rangle + \sum_l c_{Fil}\alpha_l^\dagger L_{i\sigma}|0\rangle , \tag{7}$$

and as the resonant photoionization takes place via

$$4d^{10}4f^1 L^{-1}/4d^{10}4f^0 \xrightarrow{h\nu} 4f^94f^2L^{-1}/4d^94f^1 \rightarrow 4d^{10}L^{-1} + \epsilon l,$$

the intensity is effectively given by

$$I_{Fi} \propto |\langle \Psi_I|e\,\vec{r}|\Psi_{Fi}\rangle|^2 , \tag{8}$$

where only transition matrix elements for the $4f$ emission remain nonzero. The $4f$-derived emission as a function of $E(4f^0 L^{-1} \rightarrow 4f^1 L^{-2})$ is shown in Fig. 2. One can clearly see that the $4f$ spectrum is quite different from the $4f$ component of the one-electron density of states (DOS) in the initial state.[11] Intense lines are L^{-1} final states due to the $4f$ emission while weak lines are $4f^1 L^{-2}$ final states arising from the $L \rightarrow 4f$ transition following the $4f$ emission. The
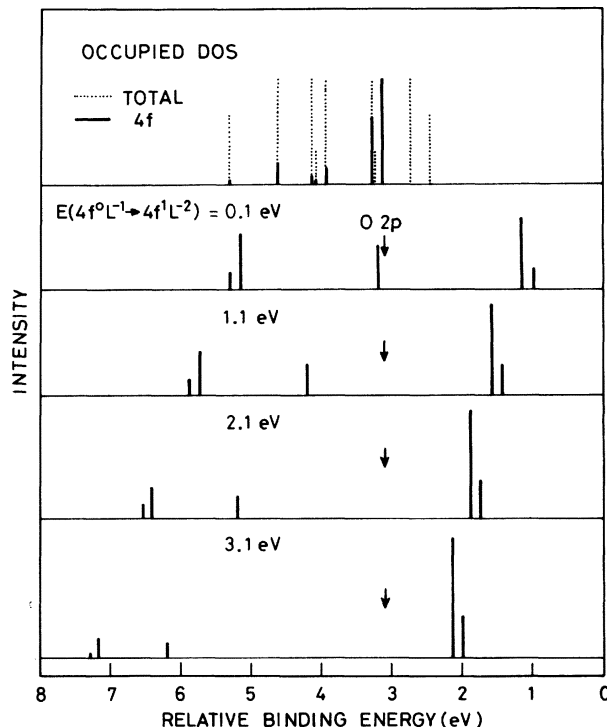

FIG. 2. $4f$-derived valence-band spectrum of CeO_2 as a function of $E(4f^0 L^{-1} \rightarrow 4f^1 L^{-2})$. The same parameters as in Fig. 1 are used. The $O\,2p$ (a_{2u} and t_{1u}) levels are shown by arrows. The top panel shows the one-electron density of states (DOS) of the CeO_8^{-12} cluster (Ref. 11).

spectrum is complicated as compared with those of Ce^{3+} compounds[10,13] due to splitting of the a_{2u}- and t_{1u}-like hole states, but gross features are not very different from Ce^{3+}. This may explain similarity between the $4f$-derived photoemission of "tetravalent" CeRh$_3$, CeRu$_2$,[6] etc., and that of trivalent intermetallic compounds. So far, resonant photoemission of CeO$_2$ has not been reported and no $4f$ satellites have been observed, although the valence-band XPS[14] seems to show the $4f$ emission overlapping the O $2p$ band.

We have shown in this Communication that CeO$_2$ is mixed valent and that nonmagnetic and insulating behavior is consistent with the presence of the $4f$ electrons if we consider the mixing of totally symmetric $4f$-electron-ligand-hole states into the pure $4f^0$ configuration. Since this mixing takes place via $4f$-ligand orbital hybridization, the total energy of the ground state is lowered as overlaps between the $4f$ and ligand orbitals ($\propto V_i$'s) become larger. This favors a smaller lattice volume as compared to Ce^{3+} compounds. We would like to recall that the above properties, nonmagnetic, small volume, $4f^0$ signals in the core-level XPS, etc., are also the case for metallic mixed-valent Ce compounds such as CeN, CePd$_3$, etc., apart from properties associated with the presence of conduction electrons. This suggests that not only the mixing $4f^0(5d6s)^m \rightarrow 4f^1(5d6s)^{m-1}$ but also $4f^0 \rightarrow 4f^1 L^{-1}$ should be considered in the metallic mixed-valent compounds. Therefore we have tried the same analysis by neglecting effects of conduction electrons for CeN, for which resonant photoemission has also been reported.[15] Both core-level[3] and $4f$ spectra have been well reproduced with ~ 0.8 of a $4f$ electron in the ground state,[16] which is again larger than the $4f$ occupancy determined from the lattice volume.[2,4] The $4f$ emission is similar to that in Fig. 2 with $E(4f^0 L^{-1} \rightarrow 4f^1 L^{-2}) = 2$–$3$ eV.

Furthermore, it is possible that the present type of mixed valency could play an essential role in α-Ce. In the case of α-Ce, $5d$ orbitals on the 12 nearest-neighbor atoms play a role of the ligand orbitals L. The $4f$ number in α-Ce is close to unity as has been revealed in many experiments,[17-19] but is not exactly one as can be seen from the $4f^0$ signal in the core-level XPS,[3] which might suggest α-Ce to be mixed valent in the same sense as CeO$_2$. It should be noted that the essential point of the present mixed-valence mechanism is not the $4f$ occupation but is the local symmetry of the electronic state of Ce losing its orbital and spin degeneracy. Therefore, in the α-γ transition, the change in the $4f$ number could be small while the transition should be a first-order one accompanied by the symmetry change of Ce $4f$. Detailed results and discussions on CeN, α-γ Ce, as well as CeO$_2$ will be published later.[16] A mechanism for the α-γ transition with volume collapse[20] will be presented there.

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[1]C. Varma, Rev. Mod. Phys. 48, 219 (1976); in *Valence Instabilities and Related Narrow-Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).

[2]J. Danan, C. de Novion, and R. Lallement, Solid State Commun. 7, 1103 (1969).

[3]Y. Baer and Ch. Zürcher, Phys. Rev. Lett. 39, 956 (1977).

[4]A. Schlegel, E. Kaldis, P. Wachter, and Ch. Zürcher, Phys. Lett. 66A, 125 (1978).

[5]W. E. Gardner, J. Penfold, T. F. Smith, and I. R. Harris, J. Phys. F 2, 133 (1972).

[6]D. J. Peterman, J. H. Weaver, and M. Croft, Phys. Rev. B 25, 5530 (1982); J. W. Allen, S.-J. Oh, I. Lindau, M. B. Maple, J. F. Suassuna, and S. B. Hagström, ibid. 26, 445 (1982); D. J. Peterman, J. H. Weaver, M. Croft, and D. T. Peterson, ibid. 27, 808 (1983).

[7]K. R. Bauchspiess, W. Boksch, E. Holland-Moritz, H. Launois, R. Pott, and D. Wohlleben, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 417.

[8]G. Krill, J. P. Kappler, A. Meyer, L. Abadli, and M. F. Ravet, J. Phys. F 11, 1713 (1981).

[9]P. Burroughs, A. Hamnett, A. F. Orchard, and G. Thornton, J. Chem. Soc. Dalton Trans., 1686 (1976).

[10]J. C. Fuggle, M. Campagna, Z. Zolnierek, R. Lässer, and A. Plateau, Phys. Rev. Lett. 45, 1597 (1980); S. Suzuki, T. Ishii,

and T. Sagawa, J. Phys. Soc. Jpn. 37, 1334 (1974).

[11]G. Thornton and M. J. Dempsey, Chem. Phys. Lett. 77, 409 (1981).

[12]W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B 23, 1266 (1981); D. D. Koelling, Solid State Commun. 43, 247 (1982).

[13]A. Fujimori, Phys. Rev. B 27, 3992 (1983).

[14]A. F. Orchard and G. Thornton, J. Electron Spectrosc. Relat. Phenom. 10, 1 (1977).

[15]W. Gudat, R. Rosei, J. H. Weaver, E. Kaldis, and F. Hulliger, Solid State Commun. 41, 37 (1982); W. Gudat, M. Iwan, R. Pinchaux, and F. Hulliger, in *Valence Instabilities*, edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 249.

[16]A. Fujimori (unpublished).

[17]D. R. Gustafson, J. O. McNutt, and L. O. Roelling, Phys. Rev. 183, 435 (1969).

[18]U. Kornstädt, R. Lässer, and B. Lengeler, Phys. Rev. B 21, 1898 (1980).

[19]N. Mårtensson, B. Reihl, and R. D. Parks, Solid State Commun. 41, 573 (1982); D. Wieliczka, J. H. Weaver, D. W. Lynch, and C. G. Olson, Phys. Rev. B 26, 7056 (1982).

[20]M. Lavagna, C. Lacroix, and M. Cyrot, Phys. Lett. 90A, 210 (1982); J. W. Allen and R. M. Martin, Phys. Rev. Lett. 49, 1106 (1982).